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THE FATE OF RADIUM IN URANIUM LEACHING AND ITS CONSEQUENT DISSOLUTION MECHANISMS

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SUMMARY

Experiments have been performed to measure the dissolution of radium isotopes Ra-226 and Ra-228 in different uranium and thorium mineral types. A considerable variety of behaviour has been observed and attempts have been to correlate the dissolution behaviour with the major elements uranium and thorium as well as with other constituents such as calcium, magnesium, barium, strontium and iron.

A second set of experiments has been carried out to investigate the dissolution of Ra-226 in pachuca leach solids from an active uranium recovery circuit. In this study, a sample of unneutralized leach solids was subjected to repetitive aqueous leaching and the relationships between species in the leachate such as sulphate, lead, barium and Ra-226 were assessed. Several interesting relationships were noted in this experiment, prompting a second experiment in which the pachuca leach solids were adjusted to pH 9 with calcium carbonate before repetitive aqueous leaching. This latter study permitted a closer simulation of Ra-226 leaching behaviour in an actual tailings site and an investigation into the effect of the presence of an excess of calcium.

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Introduction

The experiments carried out in this report have been performed under a Department of Supply and Services Contract (DSS Contract 15SQ.23241-5-1710) issued on behalf of the National Uranium Tailings Program, Dept. of Energy, Mines and Resources. The objective of this work is to identify the physical state of Ra-226 after uranium ore leaching to improve an understanding of the geochemical mechanisms controlling its dissolution in uranium tailings sites. To achieve this objective, two different types of experiments have been designed. The first experiment is an attempt to identify the host compound for Ra-226 in solids remaining in a leach pachuca of an active uranium recovery circuit. The identification has been carried out by repetitive aqueous leaching with subsequent analysis of the leachate for Ra-226 and other metals. The second experiment is an investigation of the rates at which dissolution of uranium and thorium minerals occurs under conditions similar to uranium ore processing. To accomplish this objective, different types of uranium and thorium ore minerals have been obtained and the rate of dissolution of uranium, thorium, Ra-226, Ra-228 and selected metals has been measured under standard conditions.

Since these two experiments are relatively distinct, this report is structured in two parts, Part 1 entitled 'Physical State of Ra-226' and Part 2 entitled 'Ra-226/Ra-228 Behaviour in the Leaching of Uranium and Thorium Minerals'.

1. Physical State of Ra-226

1.1. Introduction

During the leaching of uranium ore with sulphuric acid, radium-226 is thought to dissolve and subsequently re-precipitate as the sulphate. Since radium-226 cannot be present in sufficient quantities to precipitate independently, it must co-precipitate with some other insoluble material, most likely either barium or lead sulphate. Both compounds are known to be able to co-precipitate radium quantitatively in pure aqueous systems. To identify the host matrix for Ra-226, a series of leaching experiments was designed and conducted on pachuca solids from an active uranium recovery circuit. The pachuca solids consisted of the waste residue remaining after extraction of the uranium ore with sulphuric acid. When the leach experiments were completed, the leach liquor was then analyzed for Ra-226, lead, barium, iron and sulphate in an attempt to analyze the relationship between the measured constituents. In another attempt to simulate leaching behaviour in a tailings site, a sample of the pachuca leach solids was adjusted to pH 9 with calcium carbonate and hydroxide. The leaching study was then repeated to assess the impact of pH and elevated calcium content.

1.2. Experimental

1.2.1. Sample Preparation of the Pachuca Leach Solids

A sample of pachuca leach solids was kindly provided by Mr. Ted Barnes of Rio Algom Ltd. from their Elliot Lake mine. The sample had been washed briefly at the minesite to remove significant quantities of sulphuric acid.

The sample was split into two parts: One part was used for the leach study without drying or further sample preparation; the other part was dried, the moisture content determined and then the dry sample was pulverized using a ring grinder to 100% -200 mesh. The homogenized sample was used for the detailed compositional analysis of the pachuca leach solids.

1.2.2. Chemical Composition of the Pachuca Leach Solids

The dry, homogenized pulp prepared as described in Sec. 1.2.1. was dissolved in a mixture of hot concentrated nitric, perchloric and hydrofluoric acids, diluted and analyzed by inductively-coupled plasma (ICP) emission spectroscopy.

Subsamples of the leach solids were also dissolved in the same manner for Ra-226 analysis. The analysis was carried out as described in Sec. 1.2.6. Results of these analyses are listed in Table 1-1, Part A.

1.2.3. Exchangeable Ra-226 of the Pachuca Leach Solids

A subsample of the original, unprepared pachuca leach solids was tested to measure the exchangeable phase of Ra-226 as defined by Tessier et al (6). The original material was used since the exchangeable phase is certain to be dependent upon particle size. Subsample size was the equivalent of ten grams dry weight and leaching was carried out for 1 hour using 100 mls of pH 7, 1M MgCl2 solution. The leach test was performed in triplicate and the results of the Ra-226 analyses of the leachate are presented in Table 1-1, Part B.

1.2.4. Repetitive Aqueous Leach Study of the Pachuca Solids

The original unaltered pachuca solids were used for the repetitive leach study. Sample size used was the equivalent of 180 gms dry weight. The volume of water used was 1.8 L for a solid:liquid ratio of 1:10. The first study conducted was to determine the time required for equilibrium to be established in the system. Accordingly, the sample was shaken for 24 hrs. and aliquots withdrawn at the following intervals: 0.25, 0.5, 0.75, 1, 2, 4, 6, 8 and 24 hrs. The liquid aliquots were filtered through 0.45 um filters, preserved with 2% concentrated nitric acid and analyzed for lead, barium, calcium, iron and sulfate. Results are presented in Table 1-2. Since the data show that the lead and barium concentrations come quickly to equilibrium, it was decided to use a shaking time of 2 hrs.

During the leach study, one of the most important constraints was to prevent the loss of fine material during the repeated transfer and filtration processes. It is well-known that the fine material contains the highest concentration of radionuclides and so mechanical losses of fines would certainly have an adverse impact on the study. Therefore, all samples were centrifuged prior to filtration so that the supernatant liquid was clear. A minimum of suspended material was collected on the filters and this material was then rinsed back into the extraction bottles. Following filtration (0.45 u), samples were preserved with 2% concentrated nitric acid and stored in linear polyethylene bottles. The bottles had been previously acid-soaked and rinsed; bottles of this composition have been shown to be superior with respect to minimizing trace element contamination.

A total of 50 leaches was carried out in duplicate (Series A and Series B). The first ten extraction passes were analyzed as was every second extraction pass between 11 and 25, and every fifth extraction pass between 25 and 50. The extraction passes were analyzed for Pb, Ba, Ra-226, SO4 and Fe. Results of the analyses are listed in Table 1-3 (Series A) and Table 1-4 (Series B).

TABLE 1-1

A. Chemical Composition of Rio Algom Pachuca Solids

Dry Weight Basis

	%		ppm		ppm
Fe	2.67	Mo	2	Mn	17
Mg	0.09	W	<10	Cr	19
Al	3.20	Pb	345	V	13
Ca	0.10	Bi	<2	Be	0.5
Ti	0.20	Cd	<0.5	Cu	57
Na	0.18	Co	41	Ag	1.5
K	2.24	Ni	22	Sr	19
P	0.05	Ba	710		

Ra-226 (Bq/gm) 7.25

Original moisture content 10.7%

B. Exchangeable Ra-226 (Bq/gm) of Rio Algom Pachuca Solids

Analysis #1	4.08
Analysis #2	3.74
Analysis #3	3.82
Mean	3.88

TABLE 1-2

Leachability of Various Chemical Species as a Function of Time

Time (hrs)	Pb (ug/ml)	Ba (ug/ml)	Fe (ug/ml)	S04 (ug/ml)	Ca (ug/ml)	Ra-226 (Bq/1)
0.25	5.6	0.6	0.56	2.5	<0.02	141
0.50	5.9	0.6	0.46	2.5	<0.02	118
0.75	7.0	0.6	0.42	3.0	<0.02	133
1	5.6	0.6	0.30	3.0	<0.02	112
2	4.9	0.6	0.34	4.5	<0.02	109
4	6.8	0.6	0.40	4.0	<0.02	118
6	6.3	0.6	0.40	5.5	<0.02	105
8	4.9	0.6	0.40	4.5	<0.02	97
24	4.7	0.6	1.12	12.5	<0.02	110

TABLE 1-3

CHEMICAL ANALYSES OF EXTRACTIONS

SUBSAMPLE A

Extraction No.	Pb (ug/l)	Ba (ug/l)	Fe (mg/l)	SO4 (mg/l)	Ra-226 (Bq/l)
1	3300	50	24.6	410	6.04
2	4800	285	2.5	25	46.7
3	4100	955	0.3	6	121
4	3700	865	1.0	5	114
5	1300	455	0.4	3.5	48.4
6	630	675	0.4	2	23.6
7	950	655	0.7	<1	33.1
8	550	710	0.5	<1	20.2
9	240	270	0.2	<1	9.88
10	300	405	0.2	<1	8.85
11	270	385	0.5	<1	7.56
13	185	280	0.3	<1	6.36
15	145	185	0.4	1.5	3.56
17	140	210	0.2	<1	3.67
19	130	215	0.6	<1	3.04
21	120	205	0.5	1	3.00
23	95	145	0.4	<1	2.89
25	75	200	1.1	<1	3.20
30	62	130	0.2	<1	1.88
35	54	90	0.2	<1	1.17
40	38	90	0.1	<1	1.20
45	34	80	0.5	<1	1.02
50	30	60	0.1	<1	1.12

TABLE 1-4

CHEMICAL ANALYSES OF EXTRACTIONS

SUBSAMPLE B

Extraction No.	Pb (ug/1)	Ba (ug/1)	Fe (mg/1)	S04 (mg/1)	Ra-226 (Bq/1)
1	3100	45	28.4	400	5.10
2	5200	410	2.9	24	46.5
3	4100	870	0.4	6	124
4	3300	540	1.2	5	80.6
5	650	500	<0.2	2	38.0
6	1020	535	0.6	2	37.3
7	490	600	0.2	<1	20.4
8	490	565	0.4	<1	23.5
9	325	370	0.2	1.5	14.1
10	380	380	0.4	<1	12.6
11	390	350	<0.2	<1	11.0
13	250	365	0.3	<1	7.85
15	215	230	0.2	1	6.38
17	170	250	0.3	<1	6.00
19	145	180	<0.2	<1	5.31
21	110	125	<0.2	<1	3.75
23	95	110	<0.2	<1	3.20
25	90	100	0.2	<1	2.42
30	64	110	0.1	1	1.98
35	50	70	0.2	<1	1.27
40	50	110	0.2	<1	1.44
45	38	70	0.3	<1	1.12
50	36	50	0.1	<1	1.05

TABLE 1-5

CHEMICAL ANALYSES OF EXTRACTIONS

SUBSAMPLE C

(pH 9 Adjusted)

Extraction No.	Pb (ug/1)	Ba (ug/1)	Fe (mg/1)	S04 (mg/1)	Ra-226 (Bq/1)	Ca (mg/1)
1	2	75	0.01	465	3.30	200
2	5	45	0.06	26	2.19	15
3	18	25	0.10	6	1.44	9.9
4	72	40	0.55	5	2.04	8.1
5	22	45	0.13	4	1.46	10.0
6	80	40	1.20	4	1.44	9.5
7	31	45	0.18	5	3.41	7.9
8	13	35	0.07	3	2.21	9.0
9	41	30	0.22	3	1.72	7.0
10	55	35	0.32	6.5	2.56	4.8
11	104	50	0.50	4	2.58	7.3
13	72	35	0.34	3	2.09	7.0
15	55	30	0.29	2.5	1.64	7.2
17	36	30	0.16	2.5	1.25	7.0
19	16	30	0.05	2.5	0.69	6.4

1.2.5. Repetitive Aqueous Leach Study of pH 9 Pachuca Leach Solids

The leach study carried out in Sec. 1.2.4. was carried out with unneutralized pachuca leach solids direct from the leach tank. Another sample of these pachuca leach solids was then taken and adjusted to pH 9 with a slurry of calcium hydroxide. Ten grams of calcium carbonate were also added to provide an excess of calcium and to simulate the neutralization of leach solids in a tailings site. The leach study was then carried out using the same weights, volumes and times outlined in Sec. 1.2.4. Results of this study are listed in Table 1-5 (Series C).

1.2.6. Analytical Methodology

Radium-226 was determined by alpha spectroscopy following co-precipitation and purification with barium sulphate (4). Barium-133 was added as a tracer to measure the overall yield of the separation.

Barium, lead and iron were measured by atomic absorption spectroscopy and selected samples were checked by inductively-coupled plasma emission spectroscopy. Sulphate was measured turbidimetrically (7) as its barium salt.

1.3. Results and Discussion

A number of interesting features are quickly displayed in the leach study of the original pachuca solids (Table 1-3, Table 1-4, Figure 1-1). The sulphate concentration of the leach solutions is initially high (400 mg/l) and rapidly decreases to the detection limit (1 mg/l). The initial lead concentration is high and then decreases steadily with the number of extraction passes. The concentrations of barium and radium-226 are initially depressed, then rise rapidly to a peak and thereafter decrease steadily with the number of extraction passes.

A complete discussion of the significance of these results is aided by reference to experiments performed in Part 2 of this report and also by reference to other experiments performed concurrently (8,9). In Part 2 of this study, it is shown that the CANMET Standard Reference Material DH-1a, a uranium ore very similar in composition to the pachuca leach solids (Table 1-1, cf. Ref. 2), releases approximately 90% of its radium-226 during a leach with 2M perchloric acid. The same ore material, when leached with pH 1 sulphuric acid was shown (9) to have an equilibrium concentration of Ra-226 in solution that represented only about 16% of the total Ra-226. It is clear therefore that in a sulphuric acid medium, Ra-226 is being constantly removed from solution by a coprecipitation process. In perchloric acid, where very few insoluble perchlorates exist, there is evidently no chemical species being formed which would serve to remove Ra-226 from solution.

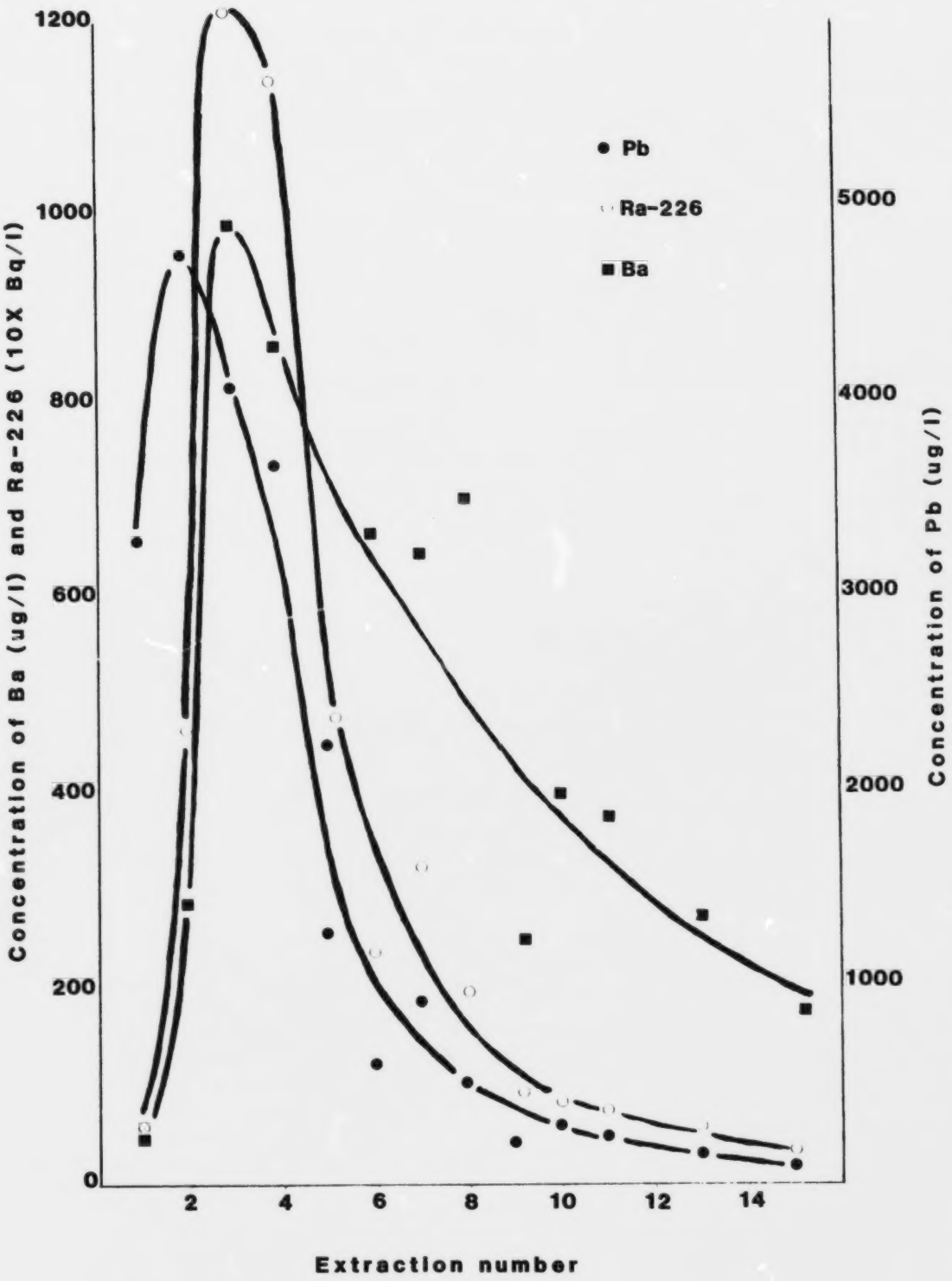

Figure 1-1: Concentration of radium-226, barium and lead as a function of extraction number (Subsample A)

It is also well-known that both lead sulphate and barium sulphate are capable of quantitatively co-precipitating Ra-226, a fact confirmed again recently (8). It is not unreasonable therefore to postulate a distribution function of Ra-226 between lead sulphate and barium sulphate, or their mixed crystals which are also likely to be present. Although the barium content of the pachuca solids exceeds that of lead, trace element leach studies of the similar ore material DH-1a (Table 2-6) show that the lead is likely to dissolve quantitatively whereas only a small portion of the barium (perhaps 15-25%) will actually dissolve and be amenable to subsequent precipitation. Therefore despite the total relative contents of barium and lead, it is likely that there will be more lead than barium available for precipitation.

For the purposes of discussion of the results of the leach study of the original pachuca solids, it is convenient to subdivide the results into three groups, extraction passes 1-5, 6-10 and 11-50. In the first group, highly significant changes in concentration occur for several chemical species. It appears initially that the sulphate concentration of the leach solution plays a critical role in controlling concentrations of barium and radium. The relevant solubility products are lead sulphate (1.9E-08), barium sulphate (1.0E-10) and radium sulphate (4.3E-11). The greater solubility of lead sulphate is shown by the fact that the lead concentration of the first extraction pass is only slightly depressed in comparison to the second pass. By contrast, concentrations of barium and radium are greatly depressed and then increase dramatically as the sulphate decreases. There is a clear relationship between barium and radium in the first four samples for each extraction series (Table 1-7, Fig. 1-1); the Ra/Ba ratio is fairly constant at 0.133 +/- 0.018 (n=8) Bq/ug. The relatively high dissolved lead content in this first group would be expected to release significant quantities of Ra-226; however it appears that this radium release comes under the control of the barium sulphate system and reprecipitates with the barium sulphate during the time that equilibrium is being established. This freshly coprecipitated radium sulphate would be held at the surface of the barium sulphate and consequently would easily redissolve as soon as the sulphate concentration is lowered, as for example, in extraction passes 3 and 4. The relative constancy of the Ra/Ba ratio is consistent with other studies (8) which show that Ra-226 leaches in proportion to the host matrix in barium sulphate.

The second group, consisting of extraction passes 6-10, shows a behaviour which is rather featureless and can be considered more or less as a transition group. Both the saturation coefficients of lead sulphate and barium sulphate (Table 1-6) as well as the interelement ratios of Ra/Ba and Ra/Pb (Table 1-7) are varying considerably in a generally decreasing fashion.

The third group, consisting of extraction passes 11-50, shows steadily declining concentrations of lead, barium and radium. If one assumes that the observed radium is being released in some proportion to both lead and barium, regardless of whether it is in direct

TABLE 1-6

Saturation Coefficients* of Lead and Barium Sulphate

Extraction No.	Lead Sulphate Subsample A	Lead Sulphate Subsample B	Barium Sulphate Subsample A	Barium Sulphate Subsample B
1	3.6	3.3	16	15
2	0.32	0.33	5.4	7.5
3	0.14	0.14	4.4	4.0
4	0.13	0.12	3.3	2.0
5	0.046	0.023	1.2	0.76
6	0.022	0.036	1.0	0.82
7	0.033	0.017	0.48	0.44
8	0.019	0.017	0.52	0.41
9	8.4E-03	0.011	0.20	0.27
10	1.1E-02	0.013	0.29	0.28
11	9.5E-03	0.014	0.28	0.25
13	6.5E-03	8.8E-03	0.20	0.27
15	5.1E-03	7.5E-03	0.13	0.17
19	4.6E-03	5.1E-03	0.15	0.13
21	4.2E-03	3.9E-03	0.15	0.091
23	3.3E-03	3.3E-03	0.11	0.080
25	2.6E-03	3.2E-03	0.15	0.073
30	2.2E-03	2.2E-03	0.095	0.080
35	1.9E-03	1.8E-03	0.066	0.051
40	1.3E-03	1.8E-03	0.066	0.080
45	1.2E-03	1.3E-03	0.058	0.051
50	1.1E-03	1.3E-03	0.044	0.036

*Note on Calculations:

Maximum metal concentrations have been calculated using the measured sulphate concentration ($\geq$2mg/1) and the appropriate solubility product. Where the sulphate concentration was <2 mg/1, the sulphate concentration has been set as equal to the metal concentration.

Some values exceed 1.00 for a number of reasons; solubility product calculations assume a neutral pH but the initial pH was less than 2 which other data (8) show will cause at least a doubling in solubility. Other factors such as ionic strength and complexation could account for further increases.

TABLE 1-7

Interelement Ratios (Bq/ug)

Extraction No.	Series A		Series B	
	Ra/Ba	Ra/Pb	Ra/Ba	Ra/Pb
1	0.121	0.002	0.113	0.002
2	0.164	0.010	0.113	0.009
3	0.127	0.030	0.143	0.030
4	0.132	0.031	0.149	0.024
5	0.106	0.037	0.076	0.058
6	0.035	0.037	0.070	0.037
7	0.051	0.051	0.034	0.042
8	0.028	0.037	0.042	0.048
9	0.037	0.041	0.038	0.043
10	0.022	0.030	0.033	0.033
11	0.020	0.028	0.031	0.028
13	0.023	0.034	0.022	0.031
15	0.019	0.025	0.028	0.030
17	0.017	0.026	0.024	0.035
19	0.014	0.023	0.030	0.037
21	0.015	0.025	0.030	0.034
23	0.020	0.030	0.029	0.034
25	0.016	0.043	0.027	0.024
30	0.014	0.030	0.018	0.031
35	0.013	0.022	0.018	0.025
40	0.013	0.032	0.013	0.029
45	0.013	0.030	0.016	0.029
50	0.019	0.037	0.021	0.029

proportion to its concentration in the host matrix or merely some percentage thereof, then it is possible to establish a number of simultaneous equations from which a number of solutions can be obtained. The general form of the equation is as follows

$$x[Pb] + y[Ba] = [Ra\text{-}226]$$

where x and y represent distribution coefficients

One solution which demonstrates good agreement between calculated and measured Ra-226 values occurs when x=0.85% and y=1.5%. A comparison of calculated and experimental Ra-226 values is presented in Tables 1-8 and 1-9. The data are also presented graphically in Fig. 1-2 in which the line drawn represents a 1:1 correlation and not necessarily the best fit for the data points.

It is also interesting to note that the sum of liberated Ra-226 over the entire leach period (approx. 4.8 Bq/gm) is fairly close to the exchangeable Ra-226 (approx. 3.9 Bq/gm) measured by the method of Tessier et al. (6).

TABLE 1-8

Comparison of Calculated Ra-226 Release from Lead Sulphate and Barium Sulphate with Experimental Measurement (Subsample A)

Ra-226 (Bq/1)

Extraction Number	Calculated Release * from $PbSO_4$	Calculated Release ** from $BaSO_4$	Total Calculated Release	Total Measured Release
11	2.3	5.8	8.1	7.6
13	1.6	4.2	5.8	6.4
15	1.2	2.8	4.0	3.6
17	1.2	3.2	4.4	3.7
19	1.1	3.2	4.3	3.0
21	1.0	3.1	4.1	3.0
23	0.8	2.2	3.0	2.9
25	0.6	3.0	3.6	3.2
30	0.5	2.0	2.5	1.9
35	0.5	1.4	1.9	1.2
40	0.3	1.4	1.7	1.2
45	0.3	1.2	1.5	1.0
50	0.3	0.9	1.2	1.1

* 0.85% of the lead concentration, converted to Bq/1
** 1.5% of the barium concentration, converted to Bq/1

TABLE 1-9

Comparison of Calculated Ra-226 Release from Lead Sulphate and Barium Sulphate with Experimental Measurement (Subsample B)

Ra-226 (Bq/l)

Extraction Number	Calculated Release * from $PbSO_4$	Calculated Release ** from $BaSO_4$	Total Calculated Release	Total Measured Release
11	3.3	5.3	8.6	11.0
13	2.1	5.5	7.6	7.9
15	1.8	3.5	5.3	6.4
17	1.4	3.8	5.2	6.0
19	1.2	2.7	3.9	5.3
21	0.9	1.9	2.8	3.8
23	0.8	1.7	2.5	3.2
25	0.8	1.5	2.3	2.4
30	0.5	1.7	2.2	2.0
35	0.4	1.0	1.4	1.3
40	0.4	1.7	2.1	1.4
45	0.3	1.0	1.3	1.1
50	0.3	0.8	1.1	1.1

* 0.85% of the lead concentration, converted to Bq/l
** 1.5% of the barium concentration, converted to Bq/l

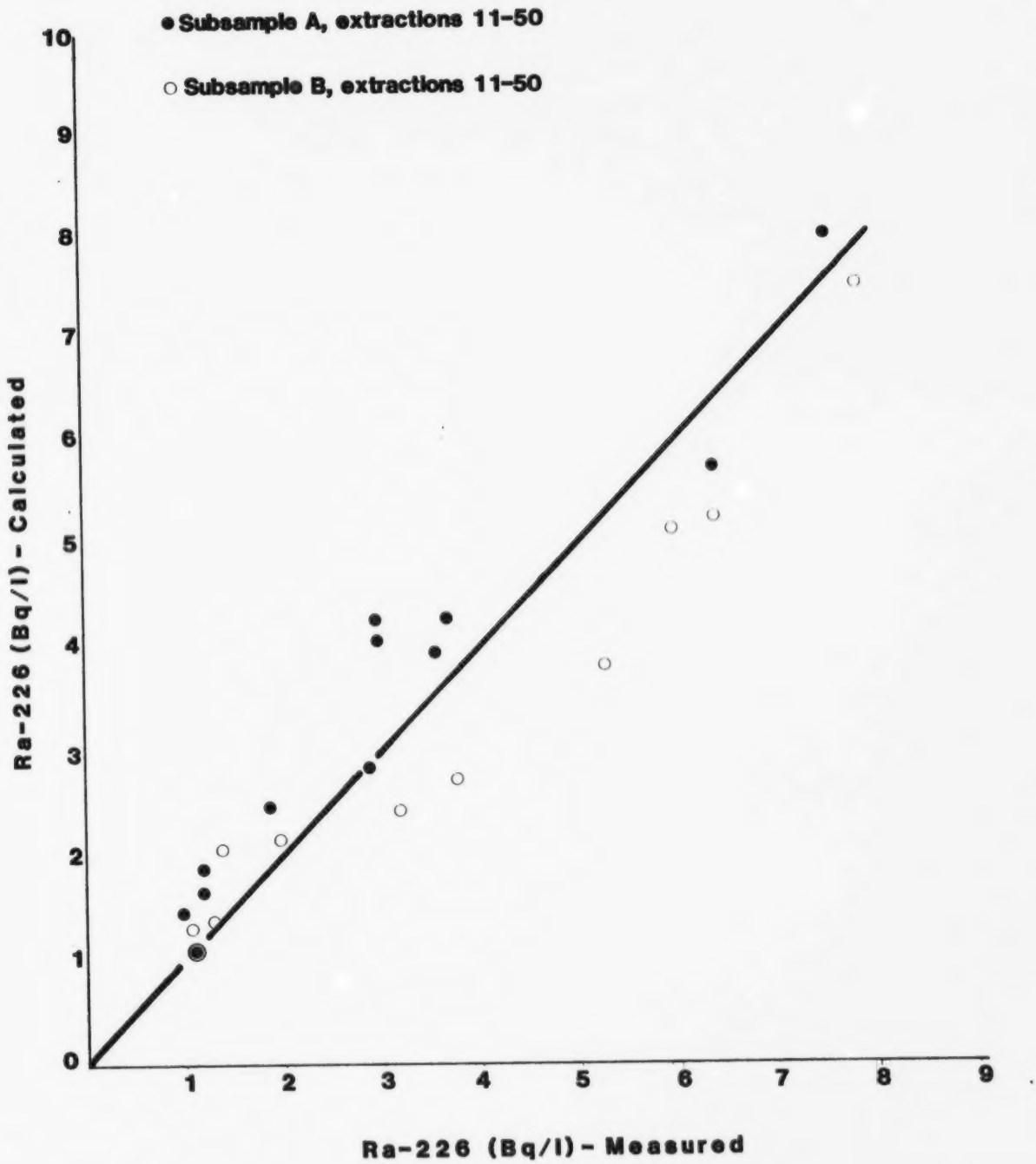

Figure 1-2: Radium-226 activity calculated as a distribution function of $PbSO_4$ and $BaSO_4$ versus measured Ra-226 values

2. Ra-226/Ra-228 Behaviour in the Leaching of Uranium and Thorium Minerals

2.1. Introduction

During leaching of uranium ore containing thorium minerals such as those encountered at Elliot Lake, Ra-226 appears to be preferentially co-precipitated with respect to Ra-228. Since there is no reason to expect a difference in chemistry between these isotopes, the explanation may be in the different leachability of uranium - and thorium - bearing minerals. To investigate this possibility, different types of uranium and thorium minerals and ores were obtained and subjected to leaching under identical conditions. Samples of the leach solutions were withdrawn at timed intervals and analyzed for uranium and Ra-226 (U-bearing minerals), thorium and Ra-228 (thorium-bearing minerals) as well as the metals Ca, Mg, Fe, Ba,Sr and Pb (all minerals).

2.2 Uranium and Thorium Mineral Types

Uranium mineral specimens of pitchblende, uraninite and brannerite were obtained. Pitchblende (1) is a cryptocrystalline variety of uraninite containing amorphous UO_2 and no thorium. The pitchblende specimen was obtained from the B.C. - Yukon Chamber of Mines and is typical of material mined at Cayzor Mines Ltd. Uraninite (1) denotes the crystalline variety of UO_2 which frequently contains variable amounts of thorium and rare earths. The uraninite specimen was obtained from Christianson Minerals of Barrie, Ontario and its origin is the Rabbit Lake Mine, Wollaston Lake, Saskatchewan. The crystalline structure of brannerite (1) is UTi_2O_6 and the brannerite specimen was also obtained from Christianson Minerals. The origin of the specimen is Crocker's Well, Australia.

In addition to these mineral specimens, an Elliot Lake ore, CANMET Standard Reference Material DH-1a, was also examined. This ore contains both uranium and thorium minerals, principally uraninite and brannerite but also traces of monazite and uranothorite. The thorium mineral britholite (1) was also studied; the sample was provided by CANMET and its origin is Oka, Quebec. Britholite is primarily a calcium-rare earth phosphate with major substitutions of thorium. It is similar to the thorium mineral monazite, a rare earth phosphate with thorium inclusions.

2.3. Experimental

2.3.1. Sample Preparation

The mineral specimens of pitchblende and brannerite were crushed, dried and pulverized in a ring grinder to 100% -200 mesh (74 um). The uraninite specimen as originally received exhibited a small amount of alteration of the primary mineral. These alteration products, identified by the supplier as kasolite and masuyite, were readily visible due to their yellow coloration. These products were removed by scraping and fracturing the samples, thus permitting isolation of the black uraninite mineral. Sample preparation was then carried out as described above. The sample of pitchblende was ashed at 1050 Deg. C. to roast any sulphides present. All prepared samples were stored in glass bottles to minimize moisture uptake and the release of radon.

2.3.2. Chemical Composition of the Mineral Specimens

Subsamples of the pitchblende, uraninite and brannerite specimens were analyzed by whole rock analysis in order to obtain detailed information on the chemical constituents. Complete analysis of the brannerite proved difficult due to difficulties in obtaining complete dissolution. Dissolution was attempted by a lithium metaborate fusion, potassium pyrosulfate fusion, $HF-HNO_3-H_2SO_4$ digestion and $HF-HNO_3-HClO_4$ digestion. In all cases insoluble residues were observed. Analyses were performed on the roasted samples where roasting was carried out. Analytical data are listed in Table 2-1. Similar data for the ore DH-1a may be found in CANMET Report 80-11E (2). The britholite sample is similar in composition to ore samples currently being circulated by CANMET and to be published in the near future under the designation OKA-2.

2.3.3. Leach Tests

Four samples were tested to study the release of U, Ra-226 and selected trace metals. Those samples included pitchblende, uraninite, brannerite and DH-1a. Specimens of pitchblende and DH-1a were tested in their original unroasted condition as well as after roasting. Three samples, roasted DH-1a, unroasted DH-1a and britholite were tested to study the release of Th, Ra-228 and selected trace metals.

In the leach tests, a solid to liquid ratio of 1:100 was used.

Ten grams of sample were added to 1 litre of 2M perchloric acid at room temperature and stirred vigorously for the duration of the leach. Aliquots of 25.0 mls were withdrawn at the following time intervals t=0 (in duplicate), 0.25 hr, 0.5 hr, 0.75 hr, 1.0 hr, 1.5 hr, 2 hr, 2.5 hr, 3, 4, 5, 6, 7, 8 and 24 hrs. All sample aliquots were analyzed for U, Ra-226, Th and Ra-228 as appropriate; in addition, those aliquots withdrawn at 0.25 hr, 1 hr, 4 hr and 24 hr were also analyzed for lead, barium, iron, calcium, magnesium and

strontium.

2.3.4. Analytical Methodology

Sulphur determinations were performed using a Leco induction furnace in which a sample is combusted and the sulphur dioxide produced is trapped and determined titrimetrically. Uranium was determined fluorimetrically as its fluoride complex following extraction into methyl isobutyl ketone from an acid-deficient aluminum nitrate solution (3). Ra-226 was determined by alpha spectroscopy following coprecipitation and purification with barium sulphate (4). Barium-133 was added as a tracer to measure the overall yield of the separation. Radium-228 was determined indirectly (4) following ingrowth and extraction of its beta- emitting daughter, Ac-228. Thorium was measured by two different techniques: Solutions from the leach of sample DH-1a were analyzed colorimetrically (5) for thorium using arsenazo III following a separation and purification with bis(ethylhexyl) phosphoric acid; however, samples from the britholite leach were analyzed by neutron activation analysis because of the high Th concentrations and the likelihood of interference by rare earth elements in the colorimetric procedure. Whole rock analyses were performed using a lithium metaborate fusion followed by a dilute nitric acid leach of the melt. The major constituents were then analyzed by inductively-coupled plasma emission spectroscopy.

2.4. Results

Analytical data generated by the experiments described above are listed in the following Tables:

Table	Title
2-1	Elemental Composition (%) of Uranium Mineral Specimens
2-2	Uranium Concentrations (ug/ml) during Dissolution
2-3	Radium-226 Activities (Bq/ml) during Dissolution
2-4	Thorium Concentrations (ug/ml) during Dissolution
2-5	Radium-228 Activities (Bq/ml) during Dissolution
2-6	Various Metal Concentrations during Dissolution
2-7	Analytical Data for Standard Reference Materials

TABLE 2-1

Elemental Composition (%) of Uranium Mineral Specimens

Constituent	Roasted Pitchblende	Uraninite	Brannerite
SiO_2	20.24	40.26	5.69
Al_2O_3	9.04	14.78	2.40
Fe_2O_3	17.26	5.71	2.00
MgO	4.03	12.02	0.58
CaO	3.52	1.88	2.09
Na_2O	0.15	0.08	0.44
K_2O	0.15	0.55	0.20
TiO_2	0.72	0.58	37.6
P_2O_5	0.91	0.23	0.12
MnO	0.32	0.09	0.06
L.O.I.	11.59	13.30	8.05
U_3O_8	26.40	10.03	21.70
PbO	1.79	0.63	2.52
BaO	0.73	0.0084	0.070
CuO	0.68	--	--
V_2O_5	0.20	--	--
ZnO	0.55	--	--
S	<0.01	0.16	0.13
ThO_2	<0.005	<0.005	6.99
Total	98.3	100.1	90.64*

* insoluble residues observed; semiquantitative analysis by NAA shows the remaining constituents to be oxides of zirconium, cerium and lanthanum.

TABLE 2-2

Uranium Concentrations (ug/ml) During Dissolution

Time (hrs)	Sample Type: Roasted Pitchblende	Sample Type: Uraninite
0	<0.1	<0.1
0	<0.1	<0.1
0.25	480	470
0.5	520	580
0.75	620	590
1.0	700	580
1.0	680	640
1.5	760	620
2.0	800	655
2.5	830	670
3	840	670
4	1000	700
4	1000	730
5	1000	720
6	1100	720
7	1100	770
8	1200	745
24	1400	800
Max. Available	2240	850

Time (hrs)	Brannerite	DH - 1a
0	<0.1	<0.1
0	<0.1	<0.1
0.25	160	5.6
0.5	180	5.8
0.75	240	6.1
1.0	260	7.1
1.0	300	7.1
1.5	330	8.0
2.0	380	8.7
2.5	460	9.0
3	470	10.0
4	560	10.0
4	590	10.0
5	640	10.0
6	700	12.0
7	750	11.0
8	790	12.0
24	1400	16.0
Max. Available	1840	26.3

TABLE 2-3

Radium-226 Activities (Bq/ml) during Dissolution

Time (hrs)	Sample Type: Roasted Pitchblende	Uraninite	Brannerite	DH-1a
0	<0.1	<0.1	<0.1	<0.01
0	<0.1	<0.1	<0.1	<0.01
0.25	9.5	9.2	3.9	--
0.5	10.1	10.8	5.1	--
0.75	--	10.8	5.8	0.06
1.0	9.4	10.1	5.4	0.07
1.5	8.3	10.2	5.6	0.09
2	9.5	9.1	8.7	0.09
2.5	8.8	--	8.2	0.09
3	9.0	10.7	9.9	0.11
4	8.6	11.1	9.8	0.11
5	10.4	10.0	10.6	0.12
6	9.9	10.9	10.9	0.16
7	8.8	--	--	0.15
8	9.9	10.9	14.2	0.16
24	11.4	10.6	20.2	0.28
Max. Available	27.7	10.5	22.7	0.315

TABLE 2-4

Thorium Concentrations (ug/ml) during Dissolution

	Sample Type	
Time (hrs)	Britholite	DH-1a
0	<1	<0.1
0	<1	<0.1
0.25	190	4.4
0.5	210	4.7
0.75	195	4.9
1.0	194	5.5
1.5	202	5.9
2	204	6.3
2.5	215	6.6
3	204	6.7
4	189	7.8
5	201	8.0
6	204	8.4
7	190	8.3
8	204	8.0
24	195	8.3
Max. Available	239	9.1

TABLE 2-5

Radium-228 Activities (Bq/ml) during Dissolution

Time (hrs)	Sample Type: Britholite	Sample Type: DH-1a
0	<0.01	<0.001
0	<0.01	<0.001
0.25	0.22	0.005
0.5	0.19	—
0.75	0.22	—
1.0	0.25	0.006
1.5	0.20	—
2	0.19	—
2.5	0.19	—
3	0.19	0.008
4	0.24	0.013
5	0.19	—
6	0.23	0.011
7	0.23	—
8	0.21	0.015
24	0.25	0.024
Max. Available	0.96	0.037

TABLE 2-6

Various Metal Concentrations During Dissolution

Sample	Leach Time (hr)	Element and Concentration					
		Pb (ppm)	Ba (ppm)	Fe (%)	Mg (%)	Ca (%)	Sr (ppm)
Pitchblende	0.25	12600	1230	0.15	0.61	0.82	127
Pitchblende	1	14300	1440	0.18	0.72	1.04	175
Pitchblende	1	13900	1360	0.17	0.68	0.99	154
Pitchblende	4	15300	1540	0.21	0.76	1.36	215
Pitchblende	4	15400	1570	0.21	0.78	1.39	220
Pitchblende	24	15300	1850	0.33	0.76	2.54	450
Pitchblende (total available)		16600	6540	12.07	2.43	2.52	450
Uraninite	0.25	3070	60	0.44	1.13	1.13	181
Uraninite	1	3310	65	0.59	1.60	1.22	186
Uraninite	1	3340	65	0.60	1.64	1.22	186
Uraninite	4	3800	75	0.88	2.55	1.23	190
Uraninite	4	3660	70	0.88	2.45	1.24	205
Uraninite	24	5560	75	2.68	5.68	1.24	205
Uraninite (total available)		5850	75	4.00	7.25	1.34	205
Brannerite	0.25	3030	260	0.09	0.05	0.29	105
Brannerite	1	4710	330	0.15	0.07	0.41	157
Brannerite	4	9340	455	0.31	0.13	0.63	225
Brannerite	24	18200	575	0.67	0.25	0.97	270
Brannerite (total available)		23400	625	1.31	0.33	1.25	300
Britholite	0.25	265	440	0.32	0.07	14.5	6990
Britholite	1	275	505	0.39	0.14	14.4	7030
Britholite	1	290	515	0.40	0.14	14.7	6770
Britholite	4	290	700	0.55	0.34	14.5	6700
Britholite	4	285	720	0.56	0.35	14.8	6780
Britholite	24	320	985	0.76	0.63	14.4	7700
DH-1a	0.25	510	20	0.25	<0.02	0.03	<2
DH-1a	1	575	20	0.27	<0.02	0.03	<2
DH-1a	4	620	25	0.32	<0.02	0.03	<2
DH-1a	24	1000	25	0.63	<0.02	0.04	<2
DH-1a (total available)		980	200	5.17	0.07	0.04	13

TABLE 2-7

Analytical Data for Standard Reference Materials

Thorium (NAA)	Added, ug	Measured, ug
	500	494
	500	520

Uranium, SRM	Certified, %	Measured, %
BL-3	1.02	1.00, 1.05
BL-5	7.09	7.20

Ra-226, NBS - traceable	Added, Bq	Measured, Bq
	0.20	0.19
	0.39	0.37
	0.79	0.82
	0.99	0.98
	1.97	1.89
	9.84	9.55
	19.7	19.4
	49.3	49.2
	98.6	97.2

Ra-228	Added, Bq	Measured, Bq
	0.20	0.18
	0.40	0.41
	0.80	0.71
	4.03	3.96

The following figures have been prepared to illustrate graphically much of the data obtained. Note that in some cases the uranium and thorium data have been converted to Bq/ml for ease of comparison with the radium-226 and radium-228 data.

Figure	Title
2-1	Uraninite - Concentration of Uranium and Ra-226 vs Time in 2M Perchloric Acid
2-2	Pitchblende - Concentration of Uranium and Ra-226 vs Time in 2M Perchloric Acid
2-3	Brannerite - Concentration of Uranium and Ra-226 vs Time in 2M Perchloric Acid
2-4	Uranium Ore DH-1a: Concentration of Uranium and Ra-226 vs Time in 2M Perchloric Acid
2-5	Effectiveness of Uranium Leaching with 2M Perchloric Acid for Different Mineral Types
2-6	Effectiveness of Ra-226 Leaching with 2M Perchloric Acid for Different Uranium Mineral Types
2-7	Uranium Ore DH-1a: Concentration of Thorium and Ra-228 vs Time in 2M Perchloric Acid
2-8	Britholite: Concentration of Thorium and Ra-228 vs Time in 2M Perchloric Acid
2-9	Effectiveness of Thorium Leaching for Different Minerals
2-10	Effectiveness of Ra-228 Leaching for Different Mineral Types
2-11	Leaching Effectiveness of Various Elements in Uraninite
2-12	Leaching Effectiveness of Various Elements in Pitchblende
2-13	Leaching Effectiveness of Various Elements in Brannerite
2-14	Leaching Effectiveness of Various Elements in DH-1a

2.5 Discussion

The uranium minerals exhibit a considerable variety of behaviour with respect to the dissolution of both uranium and radium-226. Uraninite is the mineral most easily attacked by perchloric acid with complete dissolution of radium-226 and almost complete dissolution of uranium. Brannerite is clearly the most resistant mineral and yet dissolution of uranium continues steadily and at 24 hrs. actually surpasses that of pitchblende. The behaviour of brannerite is quite distinctive in that steady dissolution of radium-226 also occurs over the 24 hr. period. Pitchblende, on the other hand, exhibits significantly different behaviour in that uranium leaching is largely complete in an 8 hr. period, and radium-226 leaching reaches an equilibrium activity immediately and remains essentially unchanged for the duration of the leach period. The uranium ore DH-1a which consists primarily of uraninite and brannerite with traces of

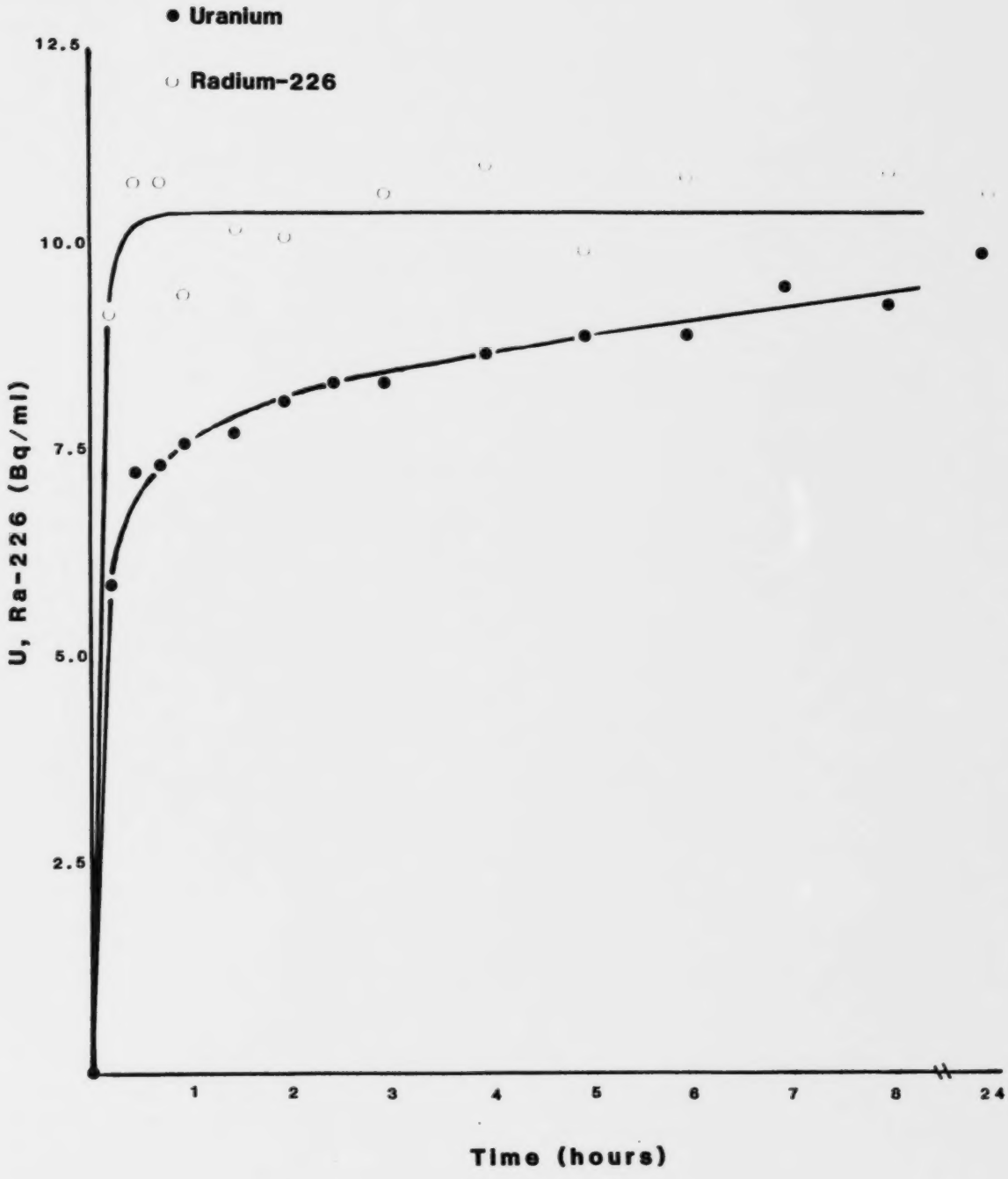

Figure 2-1: Uraninite - concentration of uranium and radium-226 vs. time in 2M $HClO_4$

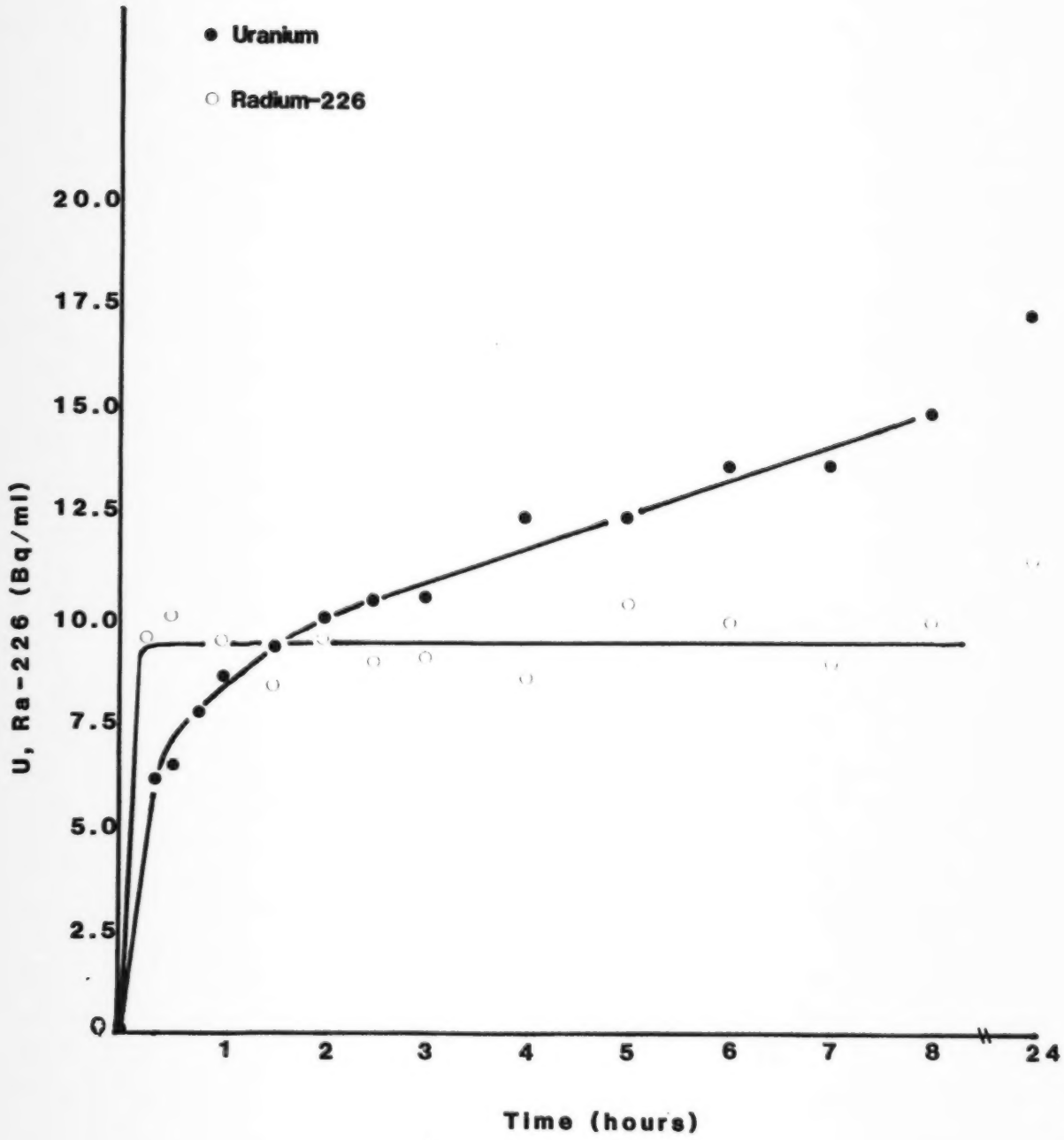

Figure 2-2: Pitchblende - concentration of uranium and radium-226 vs. time in 2M $HClO_4$

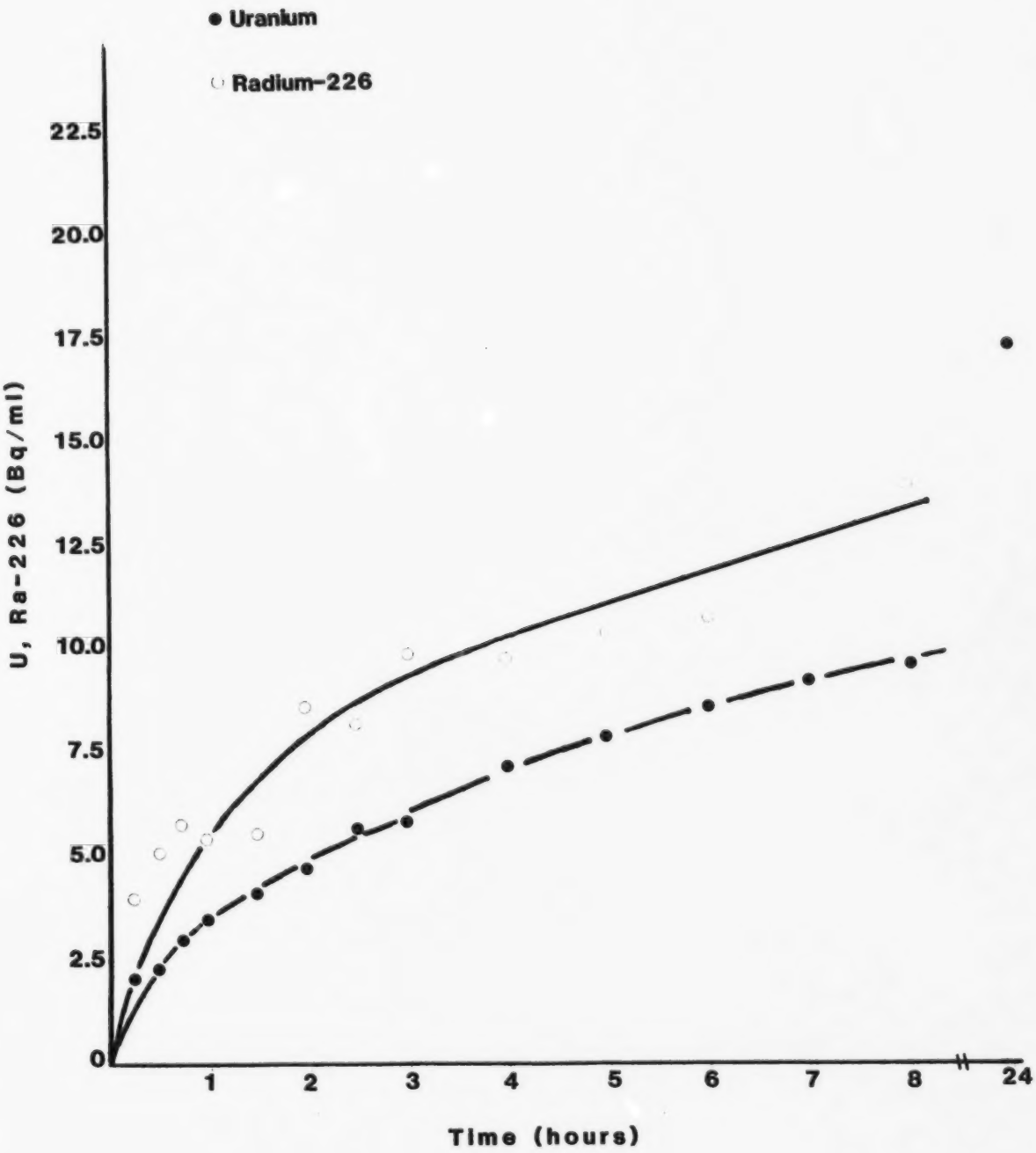

Figure 2-3: Brannerite - concentration of uranium and radium-226 vs. time in 2M $HClO_4$

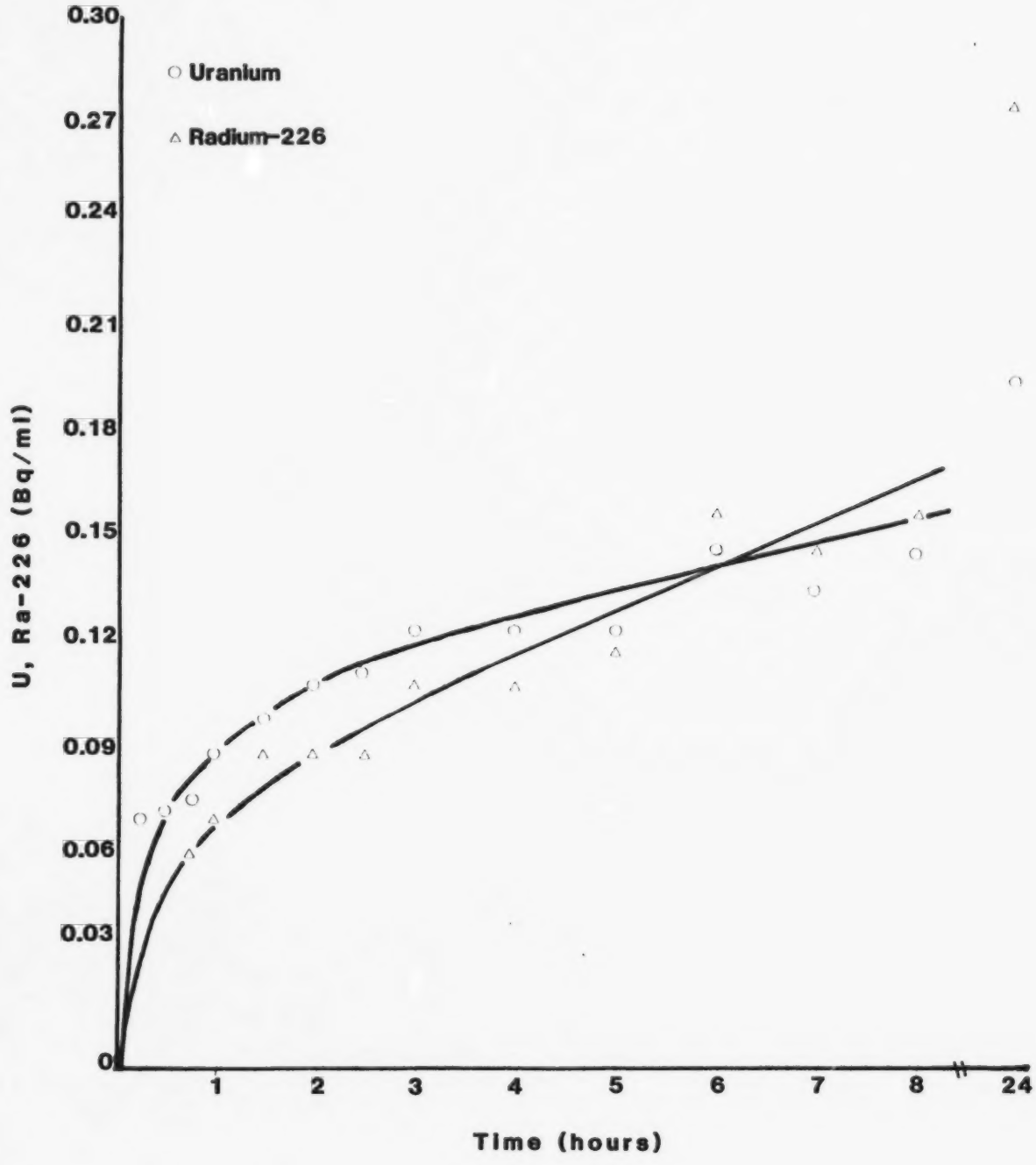

Figure 2-4: Uranium ore DH-1a - concentration of uranium and radium-226 vs. time in 2M $HClO_4$

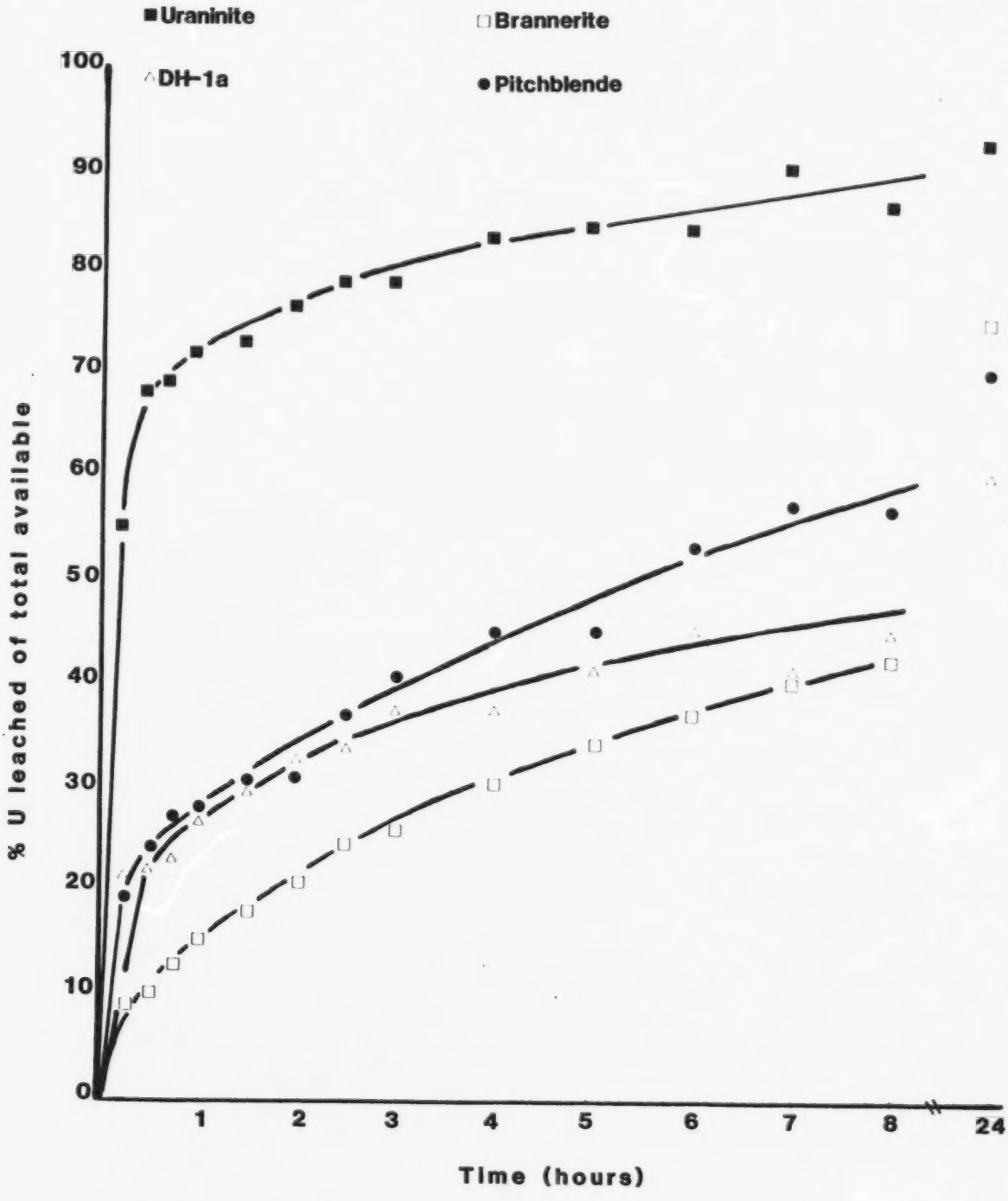

Figure 2-5: Effectiveness of uranium leaching with 2M perchloric acid for different mineral types

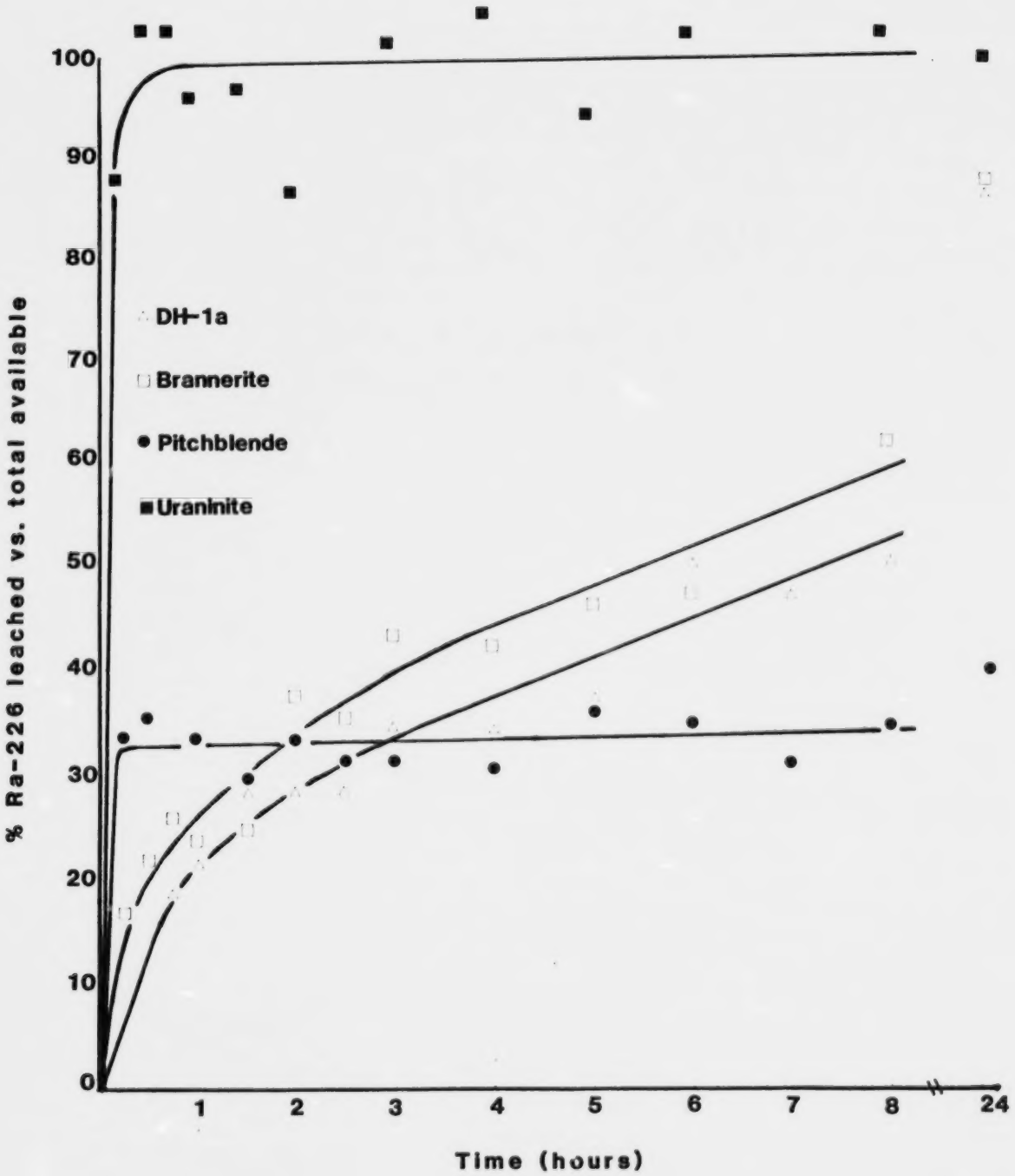

Figure 2-6: Effectiveness of Ra-226 leaching with 2M perchloric acid for different mineral types

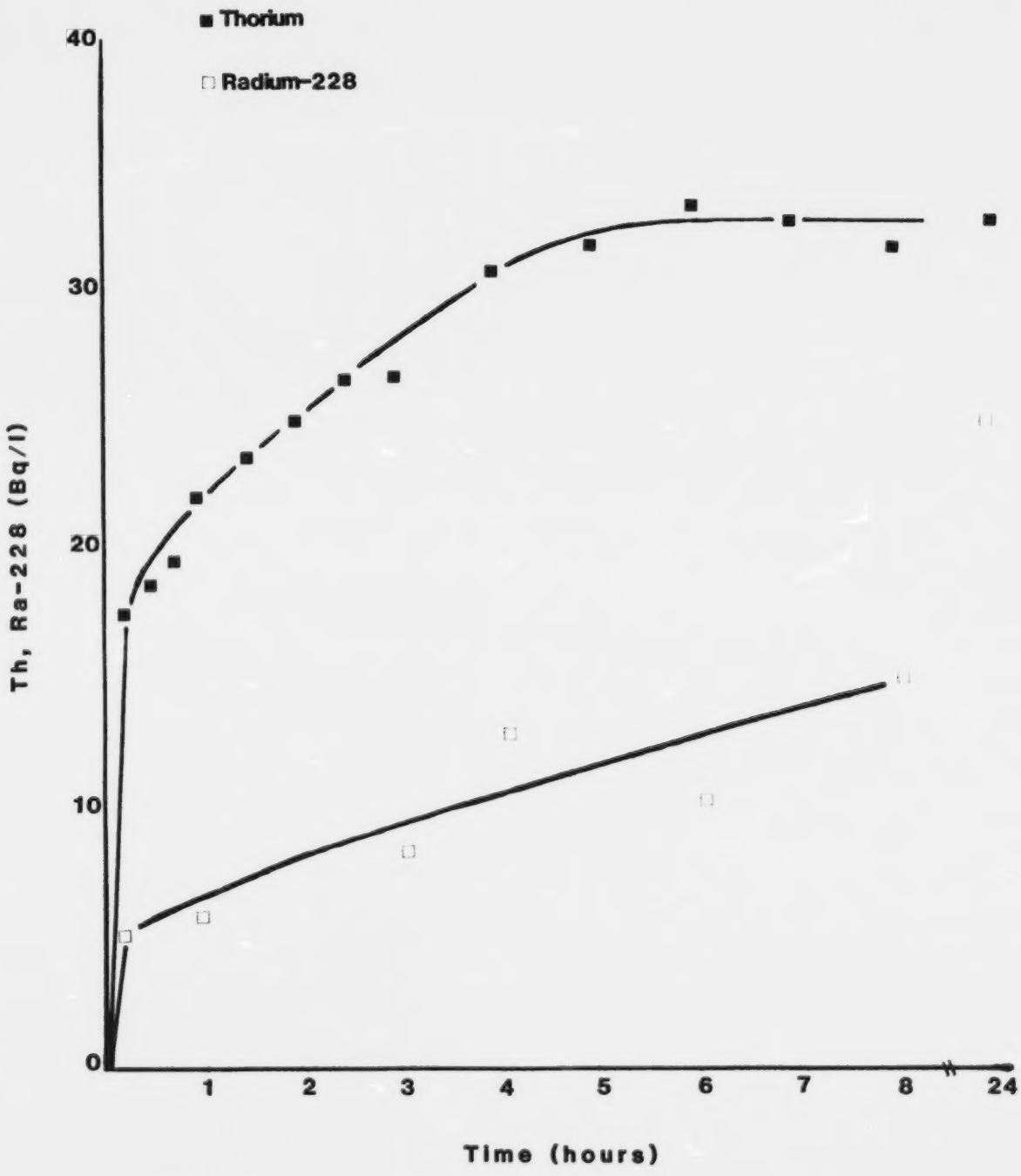

Figure 2-7: Uranium ore DH-1a - concentration of thorium and radium-228 vs. time in 2M $HClO_4$

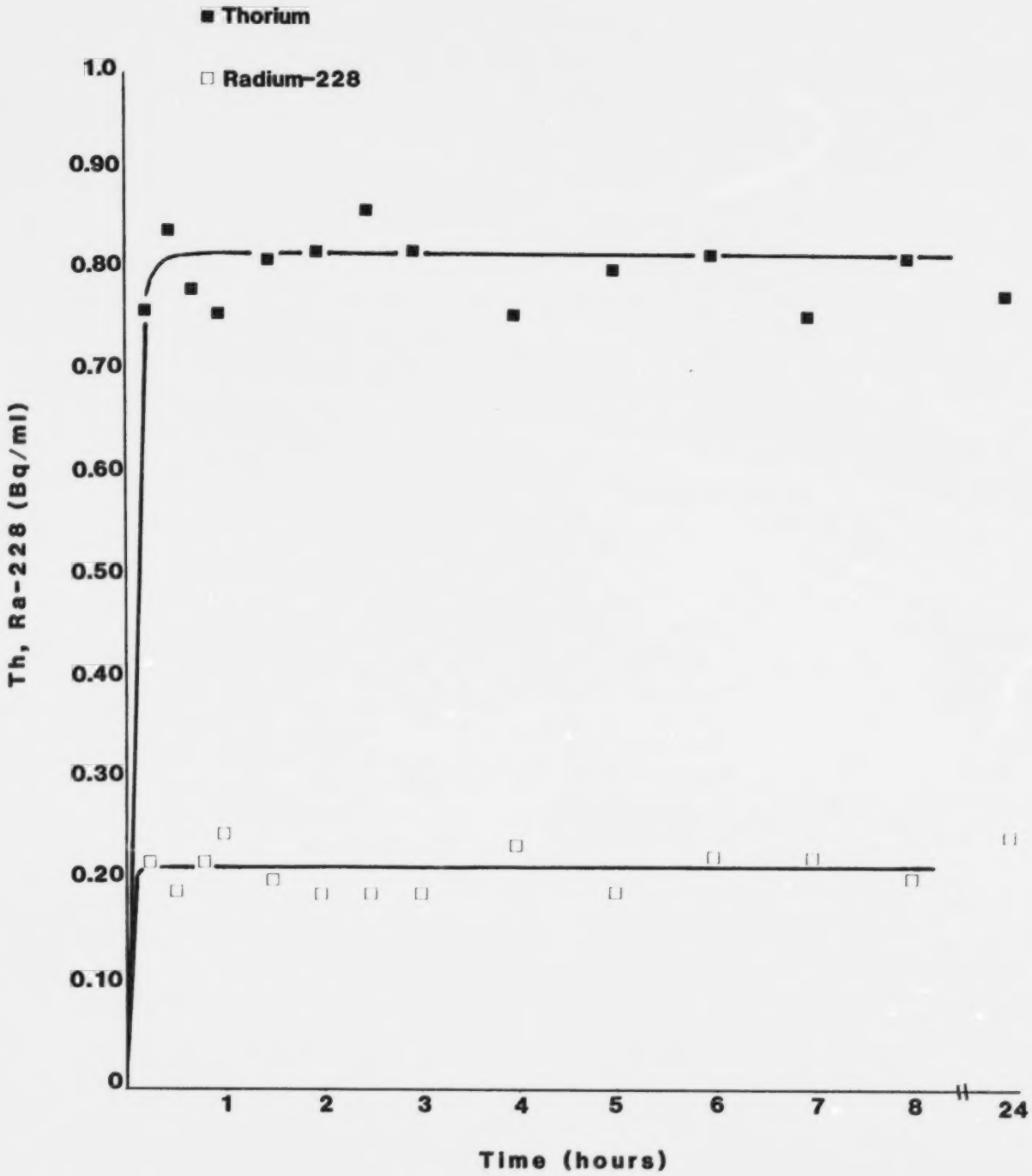

Figure 2-8: Britholite - concentration of thorium and radium-228 vs. time in 2M HClO4

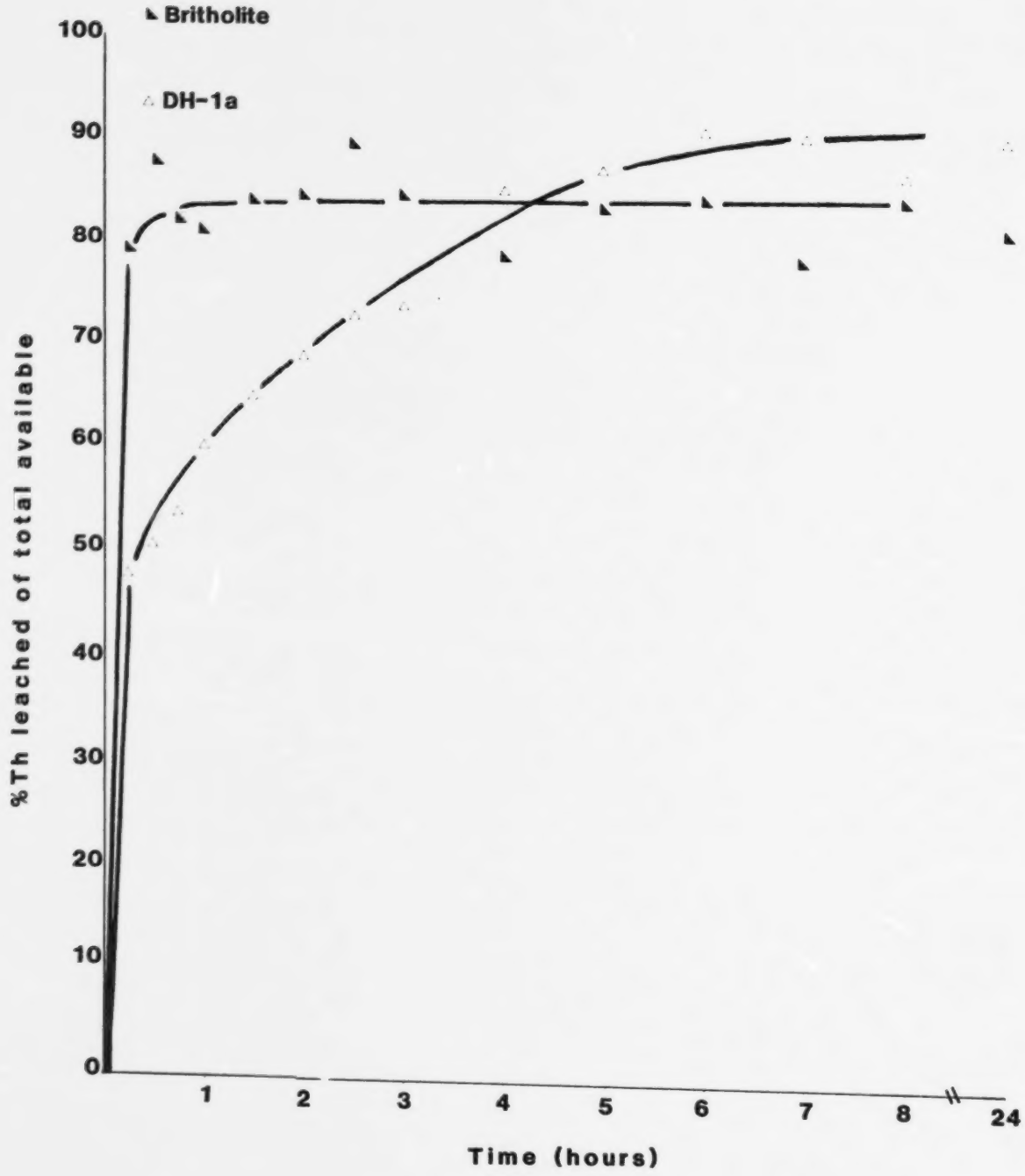

Figure 2-9: Effectiveness of thorium leaching for different minerals

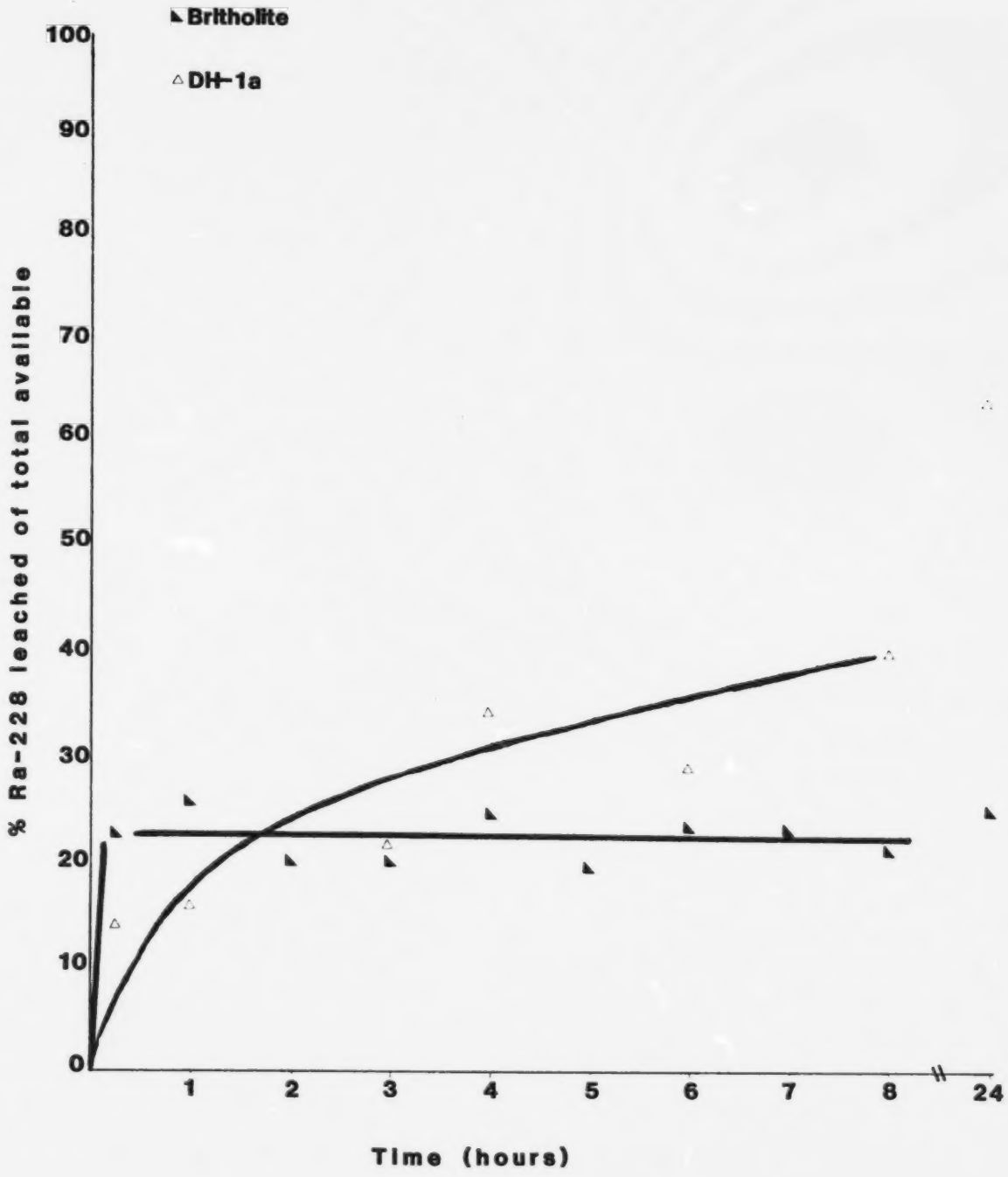

Figure 2-10: Effectiveness of Ra-228 leaching for different mineral types

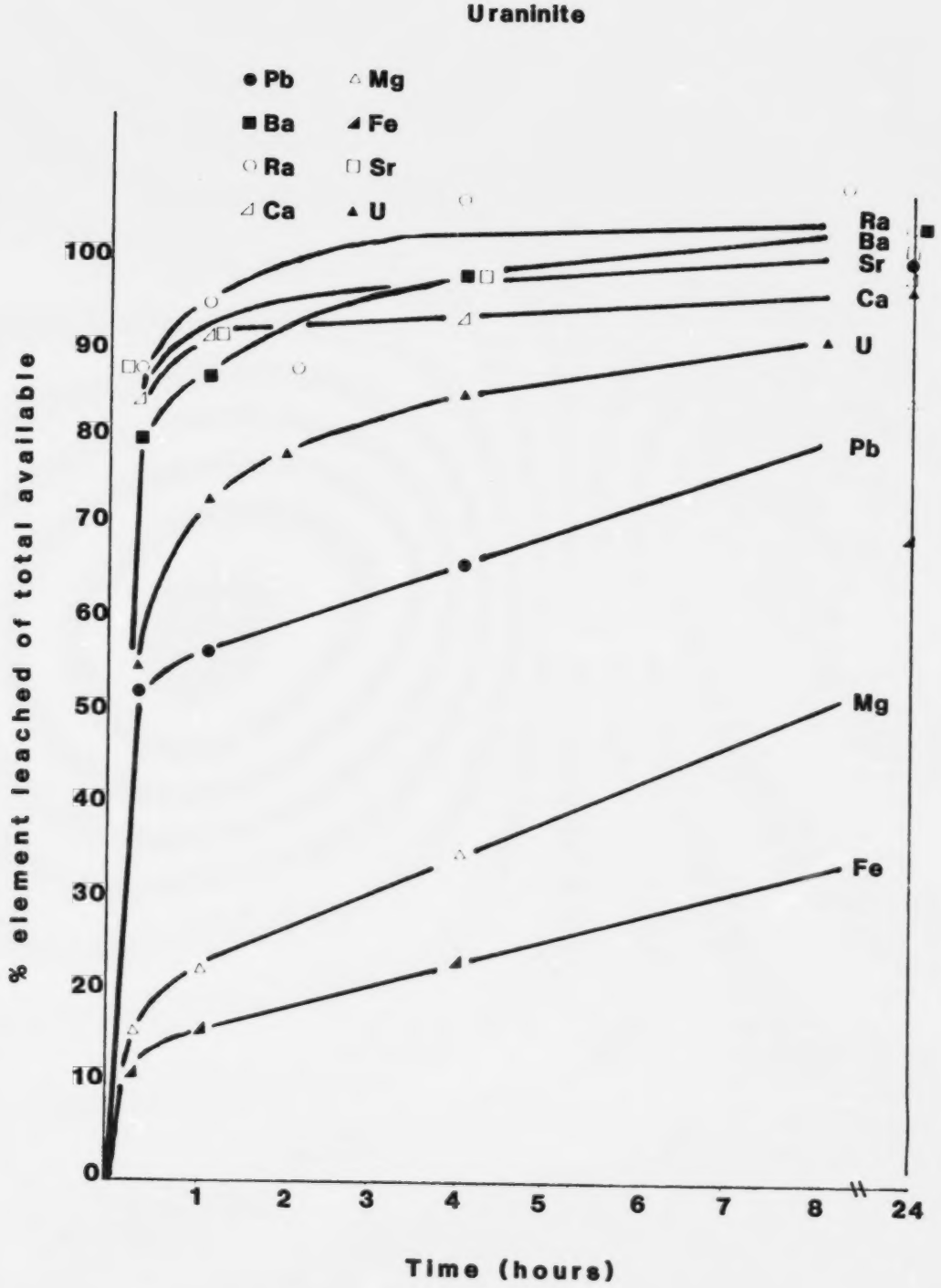

Figure 2-11: Leaching effectiveness of various elements in uraninite

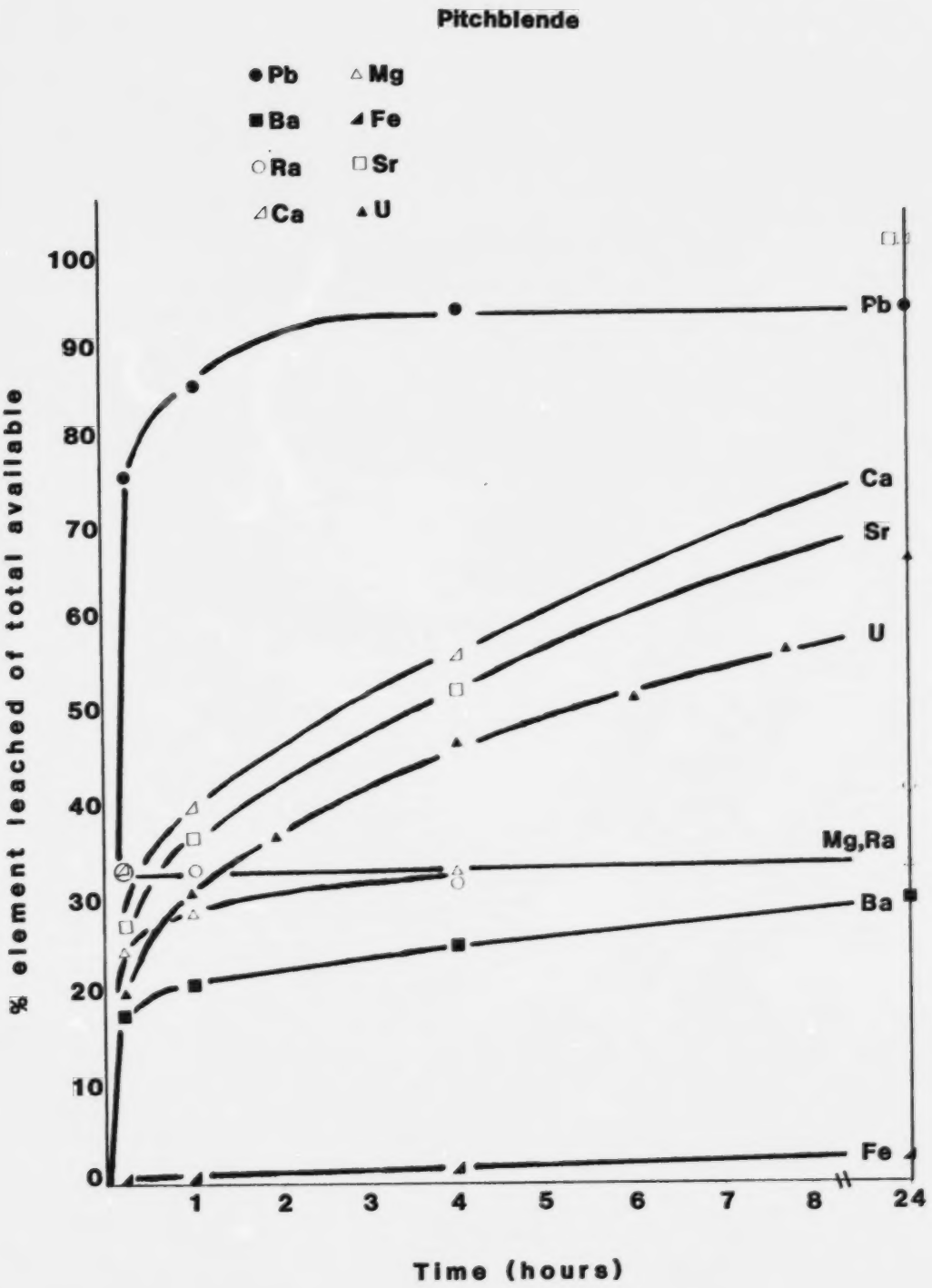

Figure 2-12: Leaching effectiveness of various elements in pitchblende

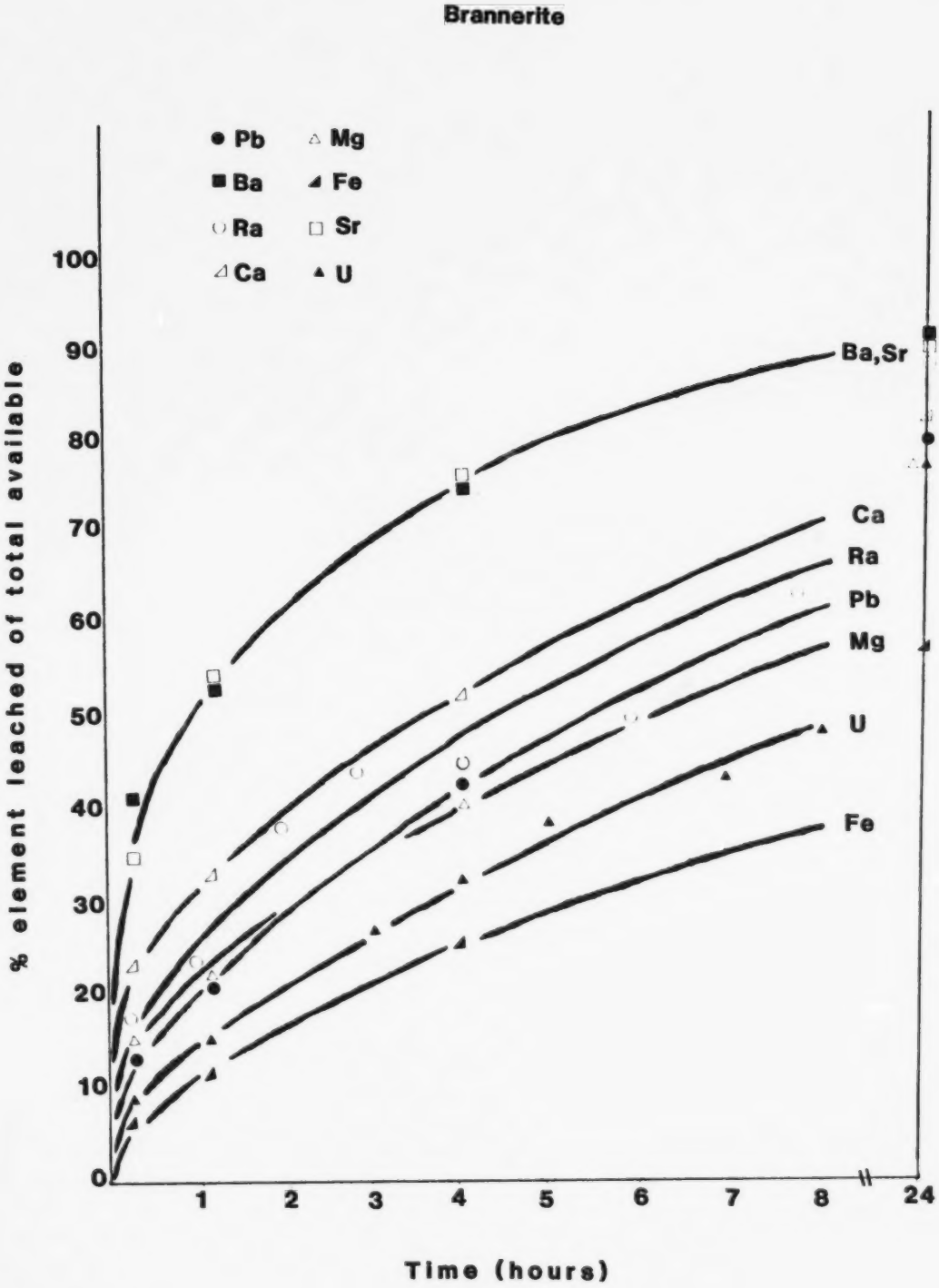

Figure 2-13: Leaching effectiveness of various elements in brannerite

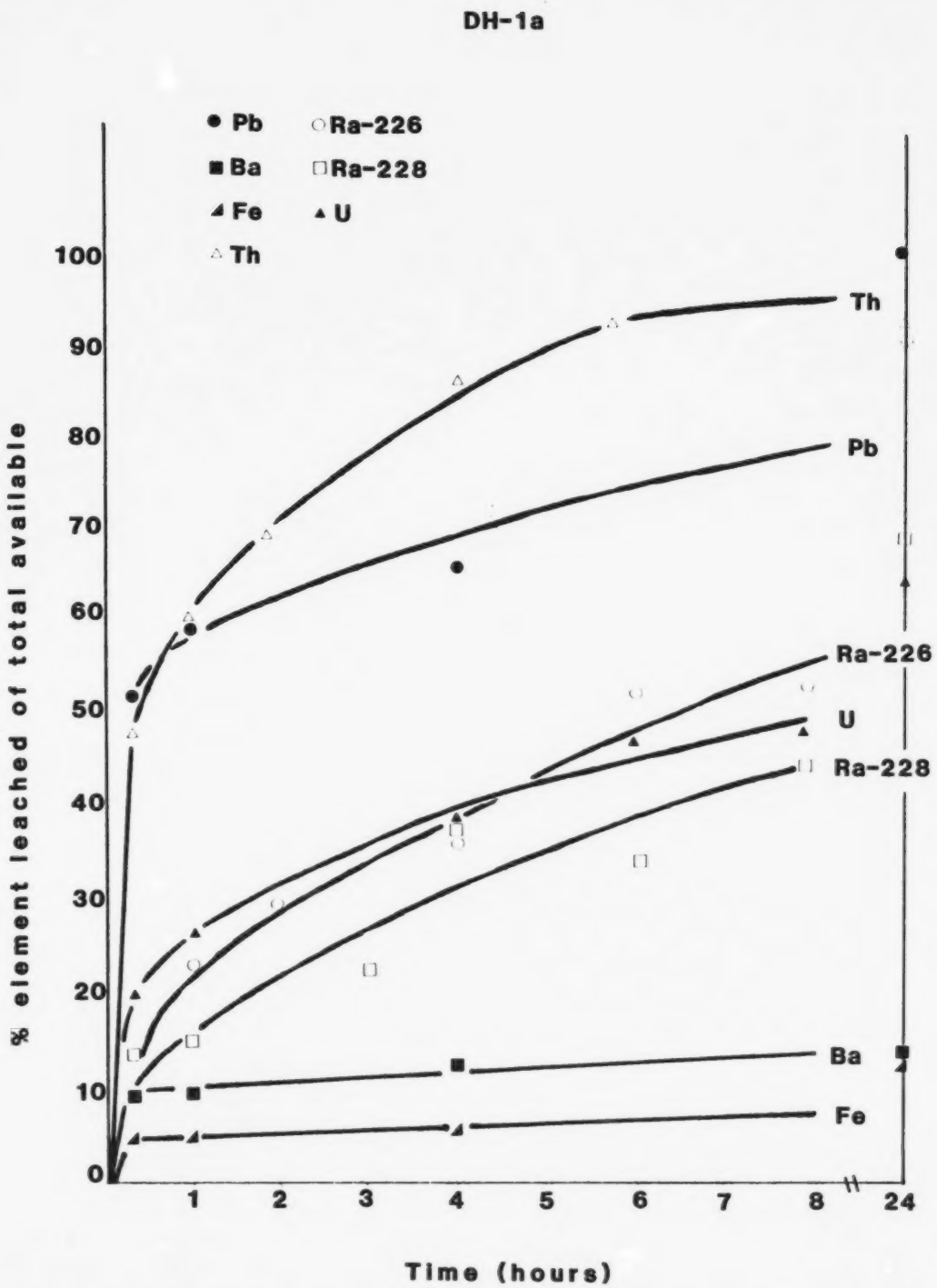

Figure 2-14: Leaching effectiveness of various elements in DH-1a

uranothorite exhibits a uranium dissolution which is less than either of its two principal minerals; on the other hand, the radium-226 extraction is similar to that exhibited by uraninite and brannerite after a 24 hr. leach period.

It is interesting to note that the extraction of radium-226 exceeds that of uranium in both the brannerite and uraninite specimens; the behaviour of radium-226 during the leach of pitchblende is curious in that the initial release of Ra-226 is greater than that of uranium, like the other minerals, but there is no subsequent increase in activity. The behaviour is similar to what one would expect if the solubility were being affected by another chemical species. It is clear from the trace element data that if there is such a controlling mechanism that it does not involve either lead or strontium since their extraction is virtually quantitative and their solutions are evidently stable. The status of barium is less clear; although only about one quarter of the total barium is solubilized over 24 hrs., there is no evidence of barium precipitation nor any obvious species which could do so.

The leaching of the thorium minerals also exhibits contrasting behaviour. The britholite specimen was particularly distinctive in that many elements, including thorium, radium-228, lead, calcium and strontium reached an equilibrium solubility within fifteen minutes and remained virtually unchanged for the balance of the leach period. Interestingly nearly four times as much thorium dissolved as did Ra-228; more than 80% of the total thorium was solubilized. The uranium ore material DH-1a contains traces of monazite and uranothorite. In this ore sample nearly 90% of the total thorium was solubilized within eight hours. By contrast, only about 65% of the total Ra-228 was solubilized, a figure significantly less than the nearly 90% of Ra-226 dissolved. The two isotopes show very similar dissolution behaviour up to 4 hours but thereafter dissolution of Ra-226 proceeds more readily.

The leaching effectiveness of various other elements in the ore and mineral specimens is presented graphically in Figs. 2-11 through 2-14. In the uraninite specimen, the dissolution of Ra-226 is similar to that of its alkaline earth family members barium, calcium and strontium but dissimilar to that of magnesium and iron. Uranium and lead are solubilized at a rate intermediate between these two extremes.

In the pitchblende specimen, Ra-226 exhibits limited solubility very similar to that of barium and magnesium and very unlike that of lead. Uranium exhibits a dissolution pattern similar to calcium and strontium.

In the brannerite specimen, all elements show a remarkably similar pattern of dissolution with availabilities between 55% and 90% after 24 hours. For the first eight hours, the dissolution rate of Ra-226 is similar to that of calcium, lead and magnesium but after 24 hours it is more similar to that of barium and strontium. The

behaviour of uranium is most similar to that of magnesium, iron and lead.

The ore sample DH-1a shows extremely varied behaviour. The radium isotopes 226 and 228 and uranium demonstrate similar behaviour up to eight hours but thereafter Ra-226 dissolves more readily. Barium and lead show considerably different behaviour in their leachability.

3. References

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